

$S=1/2$ antiferromagnetic Heisenberg chain with staggered fields: Copper pyrimidine and copper benzoate using the density matrix renormalization group for transfer matrices

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We consider the spin-1/2 antiferromagnetic Heisenberg chain in a staggered magnetic field describing materials such as copper benzoate and copper pyrimidine dinitrate. Using the density-matrix renormalization group for transfer matrices (TMRG) we calculate the magnetization of these materials at finite temperature and arbitrary magnetic field. These results are in excellent agreement with experimental data, allowing for a determination of the inhomogeneity parameter c of copper benzoate ($c = 0.043$) and copper pyrimidine dinitrate ($c = 0.11$). The TMRG approach can be applied to rather low temperatures yielding singular field and temperature dependences of susceptibilities.

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One-dimensional quantum magnets have been of theoretical and experimental interest in recent years because of the rich variety of different magnetic ground states, such as quantum critical behavior or gaps in the spin excitation spectra^{1,2,3}. The ideal spin-1/2 antiferromagnetic Heisenberg chain ($S=1/2$ AFHC) with uniform nearest neighbor exchange coupling is of particular interest, since it is exactly solvable using the Bethe ansatz (BA)^{4,5,6}. Its ground state is a spin singlet with gapless excitations and quasi-long ranged ground state correlations, hence even small perturbations can change the physical properties fundamentally.

In experimental realizations of spin chains like copper pyrimidine dinitrate $[\text{PM Cu}(\text{NO}_3)_2(\text{H}_2\text{O})_2]_n$ (CuPM) and copper benzoate $\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$ additional terms in the Hamiltonian result from the lack of inversion symmetry. As a consequence of the residual spin-orbit coupling the Dzyaloshinskii-Moriya (DM) interaction and an alternating g tensor have to be taken into account^{7,8}. This gives rise to an effective staggered field h_s perpendicular to the applied magnetic field H . The Hamiltonian is written as^{7,8}

$$\hat{H} = J \sum_i [\mathbf{S}_i \mathbf{S}_{i+1} - h_u S_i^z - (-1)^i h_s S_i^x] \quad (1)$$

with the coupling constant J , the effective uniform field $h_u = g\mu_B H/J$ and the induced effective staggered field $h_s = c h_u$. For a given field axis the effective g and the inhomogeneity parameter c are determined from the DM interaction \vec{D} and the alternating g tensor $\vec{g} = \vec{g}_u \pm \vec{g}_s$ in the following way⁹ $g = \left| \vec{g}_u \vec{H} \right| / \left| \vec{H} \right|$ and

$$c = \frac{1}{g} \left| \frac{1}{2J} \vec{D} \times \vec{g}_u \vec{H} + \vec{g}_s \vec{H} \right| / \left| \vec{H} \right|. \quad (2)$$

In essence, for materials like CuPM and Cu-benzoate, the presence of DM interaction and staggered g tensor induces new symmetry breakings with respect to the

magnetic properties. In terms of principal axes, conventionally it is distinguished between the crystallographic unit cell with the axes abc , the coordinate frame $a'bc'$, where the uniform part of the g tensor is diagonal, and the system of the principal magnetic axes $a''bc''$ ^{8,9}. For both materials the g tensor and the DM vector have been derived previously, as have the different coordinate frames^{8,9}. Hence, these quantum spin systems are perfectly suited as model compounds for a quantitatively exact comparison between theory and experiment. Correspondingly, in recent years various experimental and theoretical studies on static or dynamic properties of staggered $S=1/2$ AFHC have been carried out^{10,11,12}, even though data analysis was essentially limited to zero temperature. Therefore, in this combined theoretical and experimental study we provide a detailed investigation of the effect of temperature on thermodynamic properties of staggered $S=1/2$ AFHCs. For the first time, we derive the induced staggered magnetization for the staggered $S=1/2$ AFHC from the low temperature regime $k_B T \ll J$ up to the paramagnetic range $k_B T > J$ in fields up to saturation. Since the effective g factor and the c factor depend on the orientation of the magnetic field H with respect to the crystal axis (2), we have to calculate these physical parameters for each experimental configuration separately. For this reason, here we calculate the magnetization for different crystal alignments by use of the transfer matrix renormalization group (TMRG) method and compare these data with experimental data of CuPM¹³ and Cu-benzoate. The good agreement of numerical and experimental data allows for the determination of c and g factors.

To study thermodynamical properties at finite temperature the TMRG method provides a powerful numerical tool, because the thermodynamic limit is performed exactly and in contrast to quantum Monte Carlo techniques there is no “minus sign” problem. The idea of the TMRG method is to express the partition function Z of a one-dimensional quantum system by that of an equiva-

lent two-dimensional classical model by a Trotter-Suzuki mapping^{14,15}. For the classical model a suitable quantum transfer-matrix (QTM) can be defined which allows for the calculation of all thermodynamical quantities in the thermodynamic limit by considering solely the largest eigenvalue of this QTM. Here we use the Trotter-Suzuki mapping¹⁶ yielding $Z = \lim_{M \rightarrow \infty} \text{Tr} \left\{ [T_1(\epsilon) T_2(\epsilon)]^{M/2} \right\}$, where $T_{1,2}(\epsilon) = T_{R,L} \exp[-\epsilon H + \mathcal{O}(\epsilon^2)]$, $\epsilon = \beta/M$ with β being the inverse temperature and M a large integer number. $T_{R,L}$ denote the right- and leftshift operators, respectively. The bulk free energy is given by the largest eigenvalue Λ_0 , $f = -T \ln \Lambda_0$. Expectation values of local operators, like the homogeneous and the staggered magnetization, can be expressed in terms of the left and right eigenvectors belonging to the largest eigenvalue. For achieving lower temperatures the length of the transfer matrix is increased in imaginary time direction by an application of the infinite density matrix renormalization group (DMRG) algorithm¹⁷. In all following calculations we have retained between 64 and 100 states and used $\epsilon = 0.05$. There are no finite-size effects as the system size is strictly infinite, however numerical errors due to the discretization of the imaginary time axis and the DMRG truncation are generally within the line width used in our plots as has been checked by comparison with the exact BA data (see Fig. 1). For details of the algorithm the reader is referred to Refs.^{16,17,18,19,20}.

In the following we compare our numerical results with high-field magnetization data measured at the Laboratoire National des Champs Magnétiques Pulsés in Toulouse in pulsed magnetic fields up to $\mu_0 H = 53$ T (CuPM) and 38 T (Cu-benzoate), respectively (experimental details in Ref.¹³), and with results obtained by means of ¹³C NMR²¹. In the presence of a staggered magnetic field $h_s = c h_u$ induced by a uniform field h_u , the magnetization m is given by the superposition of the uniform m_u and the staggered m_s magnetization components^{7,8}:

$$m = m_u + c m_s, \quad (3)$$

where c is the above inhomogeneity parameter. The magnetization m can be measured experimentally. On theory side we can determine the magnetization m by using (3) and calculating the uniform m_u and the staggered magnetization m_s separately by TMRG methods.

Recently, CuPM has been identified as a $S=1/2$ AFHC, with a magnetic exchange parameter $J/k_B = (36 \pm 0.5)\text{K}$ ⁹ (in the following we use $J/k_B = 36.5\text{K}$). In the uniform $S=1/2$ AFHC model the (magnetic) saturation field is calculated according to the formula⁸

$$H_c = 4JS/g\mu_B. \quad (4)$$

The g tensor and the DM vector of CuPM have been derived from ESR measurements and single-crystal susceptibility studies⁹. In the coordinate frame $a''bc'$ the g

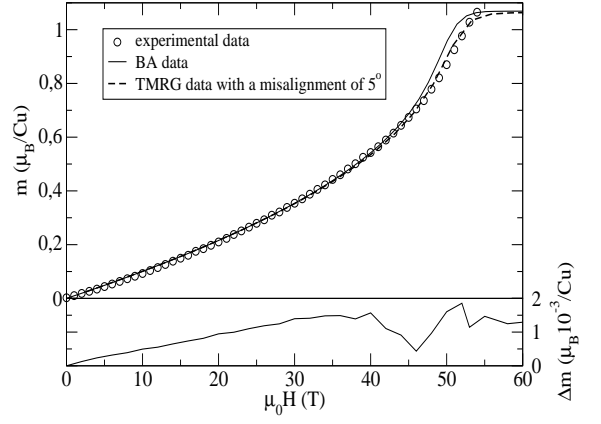


FIG. 1: Plot of theoretical (solid line) and experimental (open circles) magnetization data for CuPM at $T = 1.6$ K along the a'' direction. Dashed line shows TMRG data with a misalignment of 5° at $T = 1.6$ K. Note that deviations are strongest in the vicinity of the saturation field. Lower plot: difference between TMRG and BA data.

tensor takes the form

$$\vec{g} = \begin{pmatrix} 2.073 & 0 & 0 \\ 0 & 2.149 & \pm 0.127 \\ 0 & \pm 0.127 & 2.287 \end{pmatrix} = \vec{g}_u \pm \vec{g}_s \quad (5)$$

and the DM interaction vector reads

$$\vec{D} = 0.139J(-0.4115, 0, 0.9114). \quad (6)$$

If the magnetic field H is directed along the a'' direction of the CuPM crystal, it will behave like an ideal $S=1/2$ AFHC ($c = 0$). In this case, from (2) we obtain the effective g factor as $g = 2.14$, with saturation field $\mu_0 H_c = 50.7$ T (4). In Fig. 1 we present the magnetization curve m of CuPM as function of the magnetic field at $T = 1.6$ K along the a'' axis, as well as the difference between TMRG and the exact BA results²². Since this difference is always smaller than $2 \cdot 10^{-3}$ the TMRG results describe the exact BA results very well. Comparing the experimental data with the TMRG results we find good agreement with the uniform $S=1/2$ AFHC for magnetic fields up to $\mu_0 H < 45$ T. For higher fields the Dzyaloshinskii-Moriya interaction and the alternating g tensor may take effect on small crystal misalignments, so that CuPM does not behave like a uniform $S=1/2$ AFHC. Assuming a misalignment of 5° of the magnetic field with respect to the a'' axis¹³ the physical parameters have to be changed to $J/k_B = 36.5$ K, $g = 2.13$ and $c = 0.01$ (2). With these slight modifications the calculated magnetization curve of CuPM describes the experimental data well, see Fig. 1.

Along the c'' axis the effect due to the induced staggered field is largest⁹. According to⁸ a gap is induced $\Delta \propto h^{2/3}$ with multiplicative logarithmic corrections. At low T the magnetization receives strong contributions from the staggered component with singular behavior.

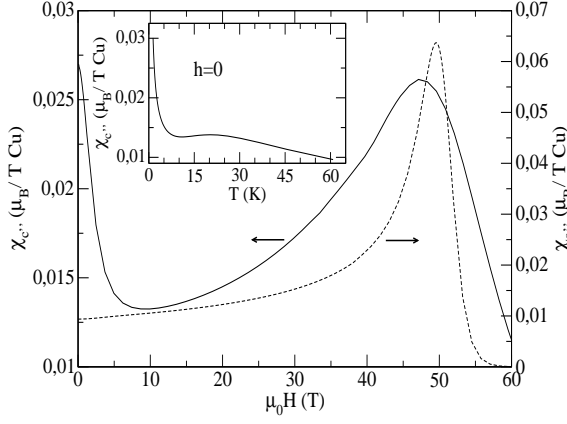


FIG. 2: Susceptibility χ of CuPM as a function of H at $T = 1.6$ K calculated by TMRG. Solid (dashed) line: susceptibility with magnetic field along c'' (a'') axis. Inset: χ of CuPM as a function of T at $h = 0$ calculated by TMRG.

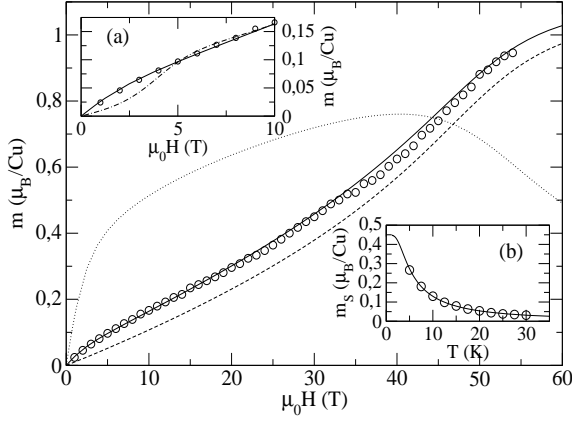


FIG. 3: Theoretical and experimental magnetization curves for CuPM at $T = 1.6$ K along the c'' direction. Solid line: magnetization m calculated for $c = 0.11$, dashed line: uniform magnetization m_u , dotted line: staggered magnetization m_s , open circles: experimental data. Inset (a) depicts the magnetization for small fields calculated by TMRG and ED (dashed-dotted line) in comparison to the experimental data, inset (b) displays the temperature dependent staggered magnetization of CuPM for a magnetic field $\mu_0 H = 9.3$ T applied along the chain axis (solid line: TMRG results; open circles: experimental data).

For $T = 0$ the dependence $m_s \propto h^{1/3}$ was found and for $h = 0$ at low T the susceptibility $\chi(T) \propto 1/T$ with multiplicative logarithmic corrections. We stress that this behavior is the result of strong correlations despite vague similarities with paramagnetic impurities. Susceptibility data are shown in Fig. 2. Note however, the direct application of DMRG¹⁰ to the Heisenberg chain with full DM-terms does not give evidences of logarithmic corrections. Along this axis we obtain the parameters $c = 0.11$ and $g = 2.19$ with saturation field $\mu_0 H_c = 49.6$ T according to (4). Figure 3 shows magnetization curves for CuPM with H along the c'' axis at temperature $T = 1.6$ K. For all

magnetic fields the magnetization calculated by TMRG is in good agreement with the experimental data. In particular at small fields, in comparison with the results of exact diagonalization (ED)¹³ the TMRG describes the experiment much more accurately, because it has no finite-size effects by construction (inset (a) of Fig. 3). We stress that the ED results were calculated for $T = 0$, whereas the TMRG results are calculated at the same finite temperatures chosen in the experiment.

For magnetic field H parallel to the chain axis⁹ of a CuPM crystal we find the parameters $c = 0.083$ and $g = 2.117$. In inset (b) of Fig. 3 we present the excellent agreement of the calculated and the measured²¹ staggered magnetization curves for magnetic field $\mu_0 H = 9.3$ T. Since these results are in good agreement with the experimental data, we verified the physical parameters for CuPM, especially $c = 0.11$ along the c'' axis with accuracy ± 0.01 . Note that this is consistent with results based on ED¹³, but rules out $c=0.08$ obtained in [23] from ESR.

Cu-benzoate is another example for a staggered $S=1/2$ AFHC, with a behavior very similar to CuPM. Only, for Cu-benzoate the coupling constant is smaller by a factor ~ 2 than for CuPM, that is $J/k_B = (19 \pm 0.5)$ K^{7,8}. In consequence, for this material, in a temperature dependent high magnetic field study, the regimes from the fully staggered one $k_B T \ll J$ up to the paramagnetic range $k_B T > J$ in fields up to saturation are accessible and can be compared to the results from TMRG calculations. From ESR measurements the g tensor in the $a''bc''$ coordinate system takes the form:

$$\vec{g} = \begin{pmatrix} 2.115 & \pm 0.0190 & 0.0906 \\ \pm 0.0190 & 2.059 & \pm 0.0495 \\ 0.0906 & \pm 0.0495 & 2.316 \end{pmatrix} \quad (7)$$

Moreover the DM interaction has been determined⁸

$$\vec{D} = J (0.13, 0, 0.02) . \quad (8)$$

Cu-benzoate will behave like a homogeneous $S=1/2$ AFHC ($c = 0$) with a coupling constant $J/k_B = 19$ K, if the magnetic field is along the a'' axis. The saturation field is calculated to $\mu_0 H_c = 26.5$ T by using $g = 2.13$ corresponding to this axis. In Fig. 4 we show the magnetization (3) as a function of the magnetic field at different temperatures. Overall, the TMRG results agree very well with the experimental data obtained in our high-field magnetization study, especially with respect to the saturation magnetization. The field induced gap of Cu-benzoate is largest for magnetic field along the c'' axis. In this case we use $J/k_B = 18.9$ K and calculate the effective g factor to $g = 2.32$, with a corresponding saturation field $\mu_0 H_c = 24.2$ T. By using (2) the c factor is determined to $c = 0.043$. The inset of Fig. 4 shows the magnetization m (3) of Cu-benzoate along the c'' axis at different temperatures. Altogether, within experimental resolution we find that the magnetization of Cu-benzoate is nicely described by TMRG results using $c = 0.043 \pm 0.01$ (covering

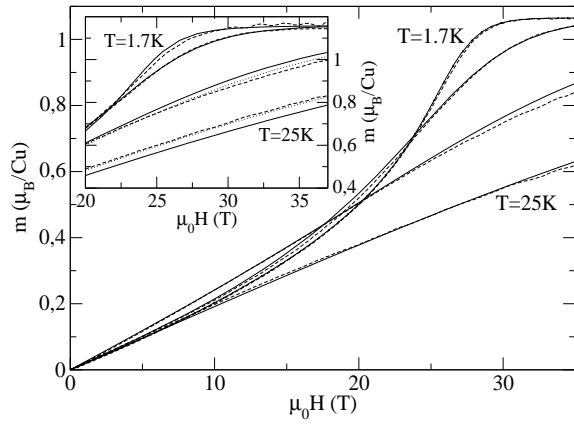


FIG. 4: Homogeneous magnetization of Cu-benzoate along a'' axis at different temperatures (1.7K, 4.2K, 12K and 25K). Solid (dashed) lines show TMRG (experimental) data. Inset: Magnetization of Cu-benzoate along c'' axis at different temperatures (1.7 K, 4.2 K, 12 K and 25 K). The dotted lines show the magnetization at $T = 12.8\text{K}$ and $T = 22.5\text{K}$ calculated by TMRG.

the value $c = 0.034$ resulting from the DM vector used in Ref.¹⁰). The somewhat larger deviations between experiment and theory at higher temperatures ($T = 25\text{ K}$) can be ascribed to a larger experimental uncertainty ($\pm 3\text{ K}$) in this temperature range.

In Fig. 5 it can be clearly seen that in the low temperature staggered regime ($1.7\text{ K} = 0.09k_B T/J$) there is a prominent staggered component, with a maximum value of about $0.6\ \mu_B/\text{Cu}$ atom at 20 T. This staggered magnetization is gradually wiped out as temperature is

increased up to $25\text{ K} = 1.3k_B T/J$, viz., the conventional paramagnetic regime.

In summary, a comparative analysis of numerical TMRG and experimental data for Cu-benzoate and CuPM at low temperatures was presented. In our comparison we found very good agreement between our numerical and experimental data. The field dependence of

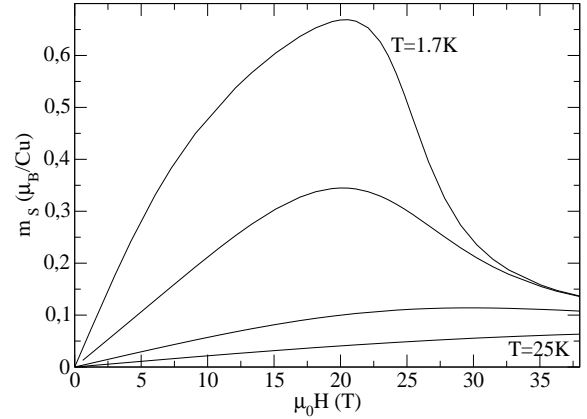


FIG. 5: Staggered magnetization of Cu-benzoate along c'' axis at different temperatures (1.7 K, 4.2 K, 12 K and 25 K).

the magnetization was found to show interesting characteristics at high fields corresponding to saturation and for low field due to quantum criticality of the $S=1/2$ AFHC.

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